

# The pesticide module of the Root Zone Water Quality Model (RZWQM): testing and sensitivity analysis of selected algorithms for pesticide fate and surface runoff<sup>†</sup>

Qingli Ma,<sup>1\*</sup> R Don Wauchope,<sup>2</sup> Kenneth W Rojas,<sup>3</sup> Lajpat R Ahuja,<sup>3</sup> Liwang Ma<sup>3</sup> and Robert W Malone<sup>4</sup>

<sup>1</sup>Environmental and Turf Services, Inc, Wheaton, MD, USA

<sup>2</sup>US Department of Agriculture, Tifton, GA, USA

<sup>3</sup>US Department of Agriculture, Fort Collins, CO, USA

<sup>4</sup>US Department of Agriculture, Ames, IA, USA

**Abstract:** The Root Zone Water Quality Model (RZWQM) is a one-dimensional, numerical model for simulating water movement and chemical transport under a variety of management and weather scenarios at the field scale. The pesticide module of RZWQM includes detailed algorithms that describe the complex interactions between pesticides and the environment. We have simulated a range of situations with RZWQM, including foliar interception and washoff of a multiply applied insecticide (chlorpyrifos) to growing corn, and herbicides (alachlor, atrazine, flumetsulam) with pH-dependent soil sorption, to examine whether the model appears to generate reasonable results. The model was also tested using chlorpyrifos and flumetsulam for the sensitivity of its predictions of chemical fate and water and pesticide runoff to various input parameters. The model appears to generate reasonable representations of the fate and partitioning of surface- and foliar-applied chemicals, and the sorption of weakly acidic or basic pesticides, processes that are becoming increasingly important for describing adequately the environmental behavior of newer pesticides. However, the kinetic sorption algorithms for charged pesticides appear to be faulty. Of the 29 parameters and variables analyzed, chlorpyrifos half-life, the Freundlich adsorption exponent, the fraction of kinetic sorption sites, air temperature, soil bulk density, soil-water content at 33 kPa suction head and rainfall were most sensitive for predictions of chlorpyrifos residues in soil. The latter three inputs and the saturated hydraulic conductivity of the soil and surface crusts were most sensitive for predictions of surface water runoff and water-phase loss of chlorpyrifos. In addition, predictions of flumetsulam (a weak acid) runoff and dynamics in soil were sensitive to the Freundlich equilibrium adsorption constant, soil pH and its dissociation coefficient.

© Published in 2004 for SCI by John Wiley & Sons, Ltd.

**Keywords:** RZWQM; sensitivity analysis; pesticide runoff; pesticide dissipation; chlorpyrifos; alachlor; atrazine; flumetsulam

## 1 INTRODUCTION

As simulation models evolve in an attempt to describe natural ecosystems in increasing detail, they incorporate more process algorithms requiring more parameters. These algorithms must be tested, first to determine simply whether they behave as expected and second by comparison with experimental data. Furthermore, the additional input parameters in many cases have to be derived, estimated or calibrated, and such estimated parameters may have different levels of uncertainty. Thus, it becomes critical to know those parameters to which the final model output is most sensitive.

Sensitivity analysis is an essential step in model parameterization, uncertainty analyses and the environmental fate model application.<sup>1,2</sup> Examples include sensitivity analyses of the CREAMS,<sup>3,4</sup> RUSLE<sup>5</sup> and HSPF models.<sup>6,7</sup> Typically the technique involves assessing the changes in a model response or output in relation to changes in individual input parameters.<sup>4,8</sup> This approach is often referred to as 'local' sensitivity analysis because it does not characterize interactions between parameters, although there are more 'global' approaches that account for parameter interactions.<sup>9,10</sup> In this stage of RZWQM development

\* Correspondence to: Qingli Ma, Senior Environmental Scientist, Environmental and Turf Services, Inc, 11141 Georgia Avenue, suite 208, Wheaton, MD 20902, USA

E-mail: qinglima@aol.com

<sup>†</sup>This article is a US Government work and is in the public domain in the USA

(Received 13 November 2002; revised version received 6 June 2003; accepted 24 July 2003)

we confine ourselves to performing local sensitivity analyses.

RZWQM is a one-dimensional, numerical model for simulating water movement and chemical transport in runoff and through a soil profile under a variety of agricultural management practice and weather scenarios at the field scale.<sup>11</sup> More than 100 parameters and input variables are needed to characterize completely a system (climate, soil, crop, chemicals and tillage). The pesticide module of RZWQM includes detailed processes for simulating pesticide fate and transport. Databases included in the model provide many default parameter values, but such values can be uncertain and unrealistic for a specific site.

Algorithm testing and sensitivity analyses here focus on five major output variables: surface water runoff, pesticide loss in surface runoff, and pesticide dissipation on crop canopy (crop residues), at the soil surface (defined in RZWQM as the top 1-cm layer) and in the soil profile (including the top 1-cm layer). RZWQM leaching prediction sensitivities are not reported here, but are discussed by Malone *et al.*<sup>12</sup> in an accompanying paper. Leaching sensitivity to various parameters has been explored thoroughly in several other pesticide fate models.<sup>8,9,13–15</sup>

## 2 MODEL DESCRIPTION

A detailed description of RZWQM has been given by Ahuja *et al.*<sup>11</sup> and the pesticide dissipation and degradation module is discussed by Wauchope *et al.*<sup>16</sup> A brief description of the major algorithms we tested is presented here.

### 2.1 Hydrology sub-model

A two-domain water flow model is used in RZWQM: soil matrix and macropores. Water infiltration into the soil matrix during rainfall and irrigation is described by a modification of the Green–Ampt equation<sup>17–19</sup> numerically modeled for each 1-cm depth increment:

$$V = \frac{K_s}{2} \cdot \frac{\tau_c + H_0 + Z_{wf}}{Z_{wf}} \quad (1)$$

where  $V$  is the infiltration rate ( $\text{cm h}^{-1}$ );  $K_s$  is the effective average saturated hydraulic conductivity of the wetting soil profile ( $\text{cm h}^{-1}$ );  $\tau_c$  is the capillary drive at the wetting front (cm), which is calculated from the unsaturated hydraulic conductivity-suction function of the wetting zone;<sup>18,20</sup>  $H_0$  is the depth of surface ponding (cm); and  $Z_{wf}$  is the depth of wetting front (cm). A viscous resistance correction factor of 2 is used in eqn (1) to correct the effect of entrapped air on  $K_s$ , based on the work of Bouwer,<sup>21</sup> Morel-Seytoux and Khanji,<sup>22</sup> and Brakensiek and Onstad.<sup>23</sup> If the average rainfall rate during a wetting interval is less than  $V$  as calculated by eqn (1),  $V$  is set equal to the rainfall rate.

The Green–Ampt equation is modified to handle the numerical problem when surface crusts/seals exist. Surface crusts/seals are assumed to be 0.5 cm thick with a model default or user-defined saturated hydraulic conductivity.

When rainfall rate exceeds the maximum soil infiltration rate, surface water runoff is produced. Runoff water is allowed to flow into macropores that are open at the soil surface, to the limit of macropore flow capacity, which is calculated by the Poiseuille's law assuming gravity flow. Water in macropores is subject to lateral infiltration into the soil matrix, which is modeled by a radial Green–Ampt type equation.<sup>24,25</sup>

Redistribution of soil water following infiltration is modeled by a mass-conservative numerical solution of the Richards' equation:<sup>26</sup>

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left[ K(h, z) \frac{\partial h}{\partial z} - K(h, z) \right] - S(z, t) \quad (2)$$

where  $\theta$  is the volumetric soil-water content ( $\text{cm}^3 \text{cm}^{-3}$ ) and  $K$  is the unsaturated hydraulic conductivity ( $\text{cm h}^{-1}$ ), both being functions of soil-water suction head,  $h$  (cm), and depth,  $z$  (cm);  $t$  is time (h);  $S(z, t)$  is a sink term for plant root water uptake and tile drain rate. The root uptake term is solved following Nimah and Hanks.<sup>27</sup>

The soil water retention relationship in eqn (2) for each soil horizon is described by a modification of the Brooks and Corey function:<sup>11,28</sup>

$$\theta(h) = \theta_s - A_1 h \quad h \leq h_b \quad (3a)$$

$$\theta(h) = \theta_r + B_1 h^{-\lambda} \quad h > h_b \quad (3b)$$

where  $\theta_s$  and  $\theta_r$  are the saturated and residual soil-water contents ( $\text{cm}^3 \text{cm}^{-3}$ ), respectively;  $h_b$  is the air-entry or bubbling suction head (cm);  $\lambda$  is the pore-size distribution index;  $A_1$  is a constant. When  $A_1$  is set to zero, eqn (3) reduces to the original Brooks–Corey function.  $B_1$  is a dependent parameter and can be determined<sup>11</sup> by the condition of continuity at  $h = h_b$ .

The hydraulic conductivity versus matric suction relationship in eqn (2) is described by<sup>11</sup>

$$K(h) = K_s h^{-N_1} \quad h \leq h_b \quad (4a)$$

$$K(h) = K_2 h^{-N_2} \quad h > h_b \quad (4b)$$

where  $N_1$ ,  $N_2$ , and  $K_2$  are constants.  $K_2$  can be determined in the same way as for  $B_1$  in eqn (3b).

Parameters for defining eqns (3) and (4) are not always available. In such a case, RZWQM uses the extended similar-media scaling technique<sup>29</sup> to estimate the  $\theta(h)$  function using soil bulk density and soil-water content at 33 kPa or 10 kPa suction head. The soil bulk density is used to calculate soil porosity ( $\Phi$ ) from which  $\theta_s$  is calculated. The reference  $\theta(h)$  function used in the scaling is the textural mean of  $\theta(h)$  function of Rawls *et al.*<sup>30</sup> The  $K_s$  value after a soil tillage is an estimate based on soil-water content at 33 kPa suction head and soil bulk density of the tilled

soil.<sup>31</sup> From the knowledge of  $K_s$  and  $\theta(h)$  function, the complete unsaturated hydraulic conductivity function,  $K(h)$ , is obtained using the capillary-bundle model as described by Campbell.<sup>32</sup>

Evapotranspiration in RZWQM uses a modification of the double-layer model<sup>33,34</sup> to calculate potential soil evaporation and crop transpiration. Major inputs are the maximum and minimum air temperatures, short-wave radiation, wind speed, relative humidity, and albedos for dry soil, wet soil, crop canopy and crop residues.

## 2.2 Pesticide sub-model

To reflect the behavior of pesticides in different parts of an agricultural ecosystem, the system is conceptually divided into four compartments: crop foliage, crop residues, soil surface, and soil sub-surface or root zone. Degradation of pesticides in each compartment is assumed to follow pseudo first-order kinetics:

$$\frac{dC}{dt} = -kC \quad \text{or, integrated:} \quad C = C_0 \cdot e^{-kt} \quad (5)$$

where  $C_0$  is the initial pesticide concentration;  $C$  is the pesticide concentration on day  $t$ ; and  $k$  is the pseudo-first-order rate constant ( $\text{day}^{-1}$ ). The values of  $k$  for the soil surface and sub-surface compartments are adjusted for temperature and soil water content as described by Walker *et al.*<sup>35,36</sup>

$$k(T, \theta) = k(T_{\text{ref}}, \theta_{\text{ref}}) \cdot \exp \left\{ \frac{E_a}{R} \left( \frac{1}{T_{\text{ref}}} - \frac{1}{T} \right) \right\} \cdot \left( \frac{\theta}{\theta_{\text{ref}}} \right)^{-\beta} \quad (6)$$

where  $k(T, \theta)$  is the rate constant at temperature  $T$  (K) and soil-water content  $\theta$ ;  $k(T_{\text{ref}}, \theta_{\text{ref}})$  is the rate constant at a reference temperature  $T_{\text{ref}}$  (K) and reference soil water content  $\theta_{\text{ref}}$ ;  $E_a$  is the degradation activation energy;  $R$  is the universal gas constant; and  $\beta$  is a constant.

Pesticides deposited on crop canopy and crop residues are subject to washoff onto the soil surface by subsequent rainfall or irrigation. This process is modeled by a power function as described by Willis *et al.*<sup>37</sup>

$$m = m_0 F_{\text{wo}} \exp(-P_{\text{wo}} I_R \Delta t) \quad (7)$$

where  $m_0$  and  $m$  are pesticide mass per unit surface area of crop canopy or crop residues ( $\mu\text{g cm}^{-2}$ ) before and after washoff, respectively;  $F_{\text{wo}}$  is the percentage of washable (dislodgeable) pesticides;  $P_{\text{wo}}$  is a rainfall washoff exponent;  $I_R$  is the rainfall rate ( $\text{cm h}^{-1}$ ), and  $\Delta t$  is the time increment (h).

Transfer of pesticides from near-surface soil to runoff water is modeled by a non-uniform mixing model,<sup>38,39</sup> assuming pesticide runoff occurring in the top 2 cm of soil:

$$M = e^{-Bz} \quad (8)$$

where  $M$  is the average degree of mixing between raindrops and soil solution integrated for each 1 cm over the top 2 cm, and  $B$  is a regression coefficient. A

value of  $4.4 \text{ cm}^{-1}$  is recommended for  $B$  by Ahuja.<sup>38</sup> Pesticide transferred into runoff is the product of the degree of mixing and pesticide concentration in soil solution at each depth increment.

Mass transfer of pesticides between soil layers in the soil matrix is modeled by a partial-piston displacement and partial-mixing approach for each 1-cm depth increment.<sup>25</sup> Pesticide displacement and mixing occur only in mesopores, but pesticide diffusion is allowed between micropores (immobile phase) and mesopores (mobile phase) according to the Fick's first law, and pesticide concentrations in both micropores and mesopores are allowed to reach equilibrium at the end of each time step.

Partitioning of pesticides between soil particles and solution can be modeled by a linear or Freundlich instantaneous equilibrium partitioning model:

$$C_s = K_d \cdot C_w = K_{\text{oc}} \cdot f_{\text{oc}} \cdot C_w \quad \text{or} \quad C_s = K_f \cdot C_w^{1/n} \quad (9)$$

where  $C_s$  and  $C_w$  are pesticide concentrations adsorbed and in solution at equilibrium;  $K_d$  and  $K_{\text{oc}}$  are partitioning coefficients based on soil and soil organic carbon fractions ( $f_{\text{oc}}$ ), and  $K_f$  and  $1/n$  are the Freundlich adsorption coefficient and exponent, respectively. Alternatively, pesticide sorption can be modeled by a two-site, equilibrium-kinetic sorption model<sup>40–43</sup> in which a fraction  $F$  of the soil sorption sites are in instantaneous equilibrium with solution as described by eqn (9) and the remaining fraction  $(1-F)$  of the sites are described by the first-order reversible adsorption kinetics:

$$\frac{dC_k}{dt} = k_{\text{ads}} \cdot [(1-F)K_d C_w - C_k] \quad (10)$$

where  $C_k$  is the pesticide concentration on kinetic sorption sites and  $k_{\text{ads}}$  is a kinetic sorption rate constant ( $\text{h}^{-1}$ ). The total pesticide sorbed is the sum of the pesticides sorbed on the two types of site.

RZWQM models sorption of partially ionized pesticides by calculating the degree of ionization based on the input of acid or base ionization equilibrium constants and the pH of the soil, with a correction factor of  $-1.8$  pH unit for surface acidity.<sup>16,44,45</sup> In the absence of adsorption constants for cations and anions, a default  $K_{\text{oc}}$  value of 10 is assigned to anions and  $10^5$  to cations. The linear, the Freundlich and the two-site sorption models may all be combined with ionization to describe weak-acid or weak-base molecule sorption.

## 3 MATERIALS AND METHODS

The results presented here are based on RZWQM version 1.0.2001.1016. Sensitivity analyses were conducted using a scenario constructed from an experimental data set collected from a  $14.5 \times 42.9 \text{ m}$  rainfall simulator plot (plot 92A) in a conventional corn (*Zea mays* L.) system. The soil was a Tifton

loamy sand (fine-loamy, kaolinitic, thermic Plinthic Kandiudults). Details of the field study have been reported elsewhere.<sup>46,47</sup> Briefly, the study involved applying six artificial rainfalls (25 mm h<sup>-1</sup> for 2 h each) to the field using a large-scale rainfall simulator<sup>48</sup> immediately after pesticide applications at various stages of crop growth. Runoff flows were measured and runoff water was sampled for pesticides and sediment. Chlorpyrifos was applied broadcast at a rate of 1.12 kg AI ha<sup>-1</sup> 1 day before each of the rainfall simulation Events 3, 4, and 5. These three applications were made ranging from post-emergence through mature crop. Atrazine and alachlor were surface broadcast just before planting corn at 1.6 and 1.26 kg AI ha<sup>-1</sup>, respectively. A weakly acidic herbicide, flumetsulam, was also modeled (though it was not used experimentally), assuming it was surface broadcast at a rate of 0.075 kg AI ha<sup>-1</sup> at the same time as atrazine and alachlor applications. Corn residues of 10 tonne ha<sup>-1</sup> were assumed to exist initially at the soil surface.

Measured soil and soil hydraulic properties (Table 1) were used to parameterize the hydrology sub-model of RZWQM. The measured soil water content at 33 kPa suction head, soil bulk density, saturated hydraulic conductivity and soil particle-size distribution were used to estimate parameters for describing the soil-water retention (eqn (3)) and hydraulic conductivity (eqn (4)) functions according to the extended similar-media scaling technique.<sup>29</sup> As such, all evaluations were on the basis of such soil hydrology estimations.

Tifton loamy sand is a crusting soil<sup>49,50</sup> and surface crusts/seals were observed during the study, but the saturated hydraulic conductivity of the surface crusts was not measured. For the purposes of this study we simply calibrated the model by minimizing the differences between measured and predicted surface water runoff total for all six artificial rainfall events, with special treatments for Events 1 and 2, as described below; a surface seal saturated hydraulic conductivity of 0.007 cm h<sup>-1</sup> gave reasonable surface water runoff prediction.

Even with seals, RZWQM initially predicted no runoff from Events 1 and 2 because the tillage operations immediately before these events (plowing

and bed formation on the day of Event 1; planting and rototilling<sup>47</sup> on the day before Event 2) caused the model to destroy seals. A large rainfall event falling on such freshly tilled soil will initially reconsolidate and reseal the soil and, as rainfall continues, runoff will eventually be generated. However, RZWQM adjusts seals and soil bulk density only on a daily time step. Thus, within-storm reconsolidation will not be simulated until the end of the day—an example of the limitations of daily time step models.

We artificially generated surface seals before Events 1 and 2. To form seals before Event 1 we artificially moved the major tillage events—moldboard plowing and bed formation—back 2 days, prior to a moderate natural rainfall event that occurred before the simulated rainfall event. To form seals before Event 2 we moved the planting/rototilling tillage back 1 day, and inserted a small (0.3 mm) rain on the day before Event 2—just enough to seal the surface. These manipulations gave reasonable water runoff simulation based on which we examined the model sensitivities.

Input parameter values for the pesticides are given in Table 2. The  $K_{oc}$  and half-life values for chlorpyrifos, atrazine and alachlor were obtained from Wauchope *et al.*<sup>51</sup> and Getzin.<sup>52</sup> We used the two-site, equilibrium-kinetic sorption model for chlorpyrifos sorption and assumed 30% of the soil sorption sites were 'kinetic' diffusion controlled. The kinetic sorption rate constant for chlorpyrifos was estimated<sup>53</sup> as 0.002 h<sup>-1</sup>. The  $K_{oc}$  values for flumetsulam and its deprotonated anion were obtained from Fontaine *et al.*<sup>54</sup> The Freundlich equation (eqn (9)) was used for all pesticides with  $1/n$  being equal to 1 (Table 2). Pesticide half-life and washoff parameter values on crop residues were assumed to be the same as those on crop canopy (Table 2). Measured meteorological data at the experimental site were used in the simulations. These data were used as base values to conduct sensitivity analyses for predictions of pesticide washoff and dissipation in different compartments including corn canopy (crop residues), soil surface and the root zone, and mass transfer (washoff) between compartments.

To examine RZWQM's predicted pH dependence of sorption of the ionizable herbicides (atrazine and

**Table 1.** Means ( $n = 24$ ) of selected soil and soil hydraulic properties of Tifton loamy sand<sup>a</sup>

Depth (m)	Sand	Silt	Clay	OC	$\theta_f$	$\theta_r$	pH	$\rho$	$K_s^g$
	(%)				(m <sup>3</sup> m <sup>-3</sup> )	(m <sup>3</sup> m <sup>-3</sup> )		(mg m <sup>-3</sup> )	(cm h <sup>-1</sup> )
0.0–0.29	84.6	9.3	6.1	0.79	0.099	0.043	4.8	1.64	12.05
0.29–0.62	63.4	11.4	25.2	0.34	0.244	0.150	4.6	1.69	4.54
0.62–0.92	62.9	11.0	26.1	0.24	0.272	0.161	5.0	1.66	3.52
0.92–1.11	62.3	10.6	27.1	0.12	0.294	0.177	5.5	1.68	3.35
1.11–1.43	60.4	11.8	27.8	0.02	0.303	0.187	5.1	1.69	0.49
1.43–1.60	48.3	15.8	35.9	0.01	0.375	0.225	4.3	1.65	0.19

<sup>a</sup> OC is soil organic carbon content;  $\theta_f$  and  $\theta_r$  are volumetric soil water contents at 33 kPa and 1500 kPa suction head, respectively;  $\rho$  is soil bulk density; and  $K_s^g$  is the geometric mean of the saturated hydraulic conductivities. Soil pH was measured using 0.01 M CaCl<sub>2</sub> solution.

**Table 2.** Selected properties of the tested pesticides

Pesticide	Chlorpyrifos	Alachlor	Atrazine	Flumetsulam
Soil (neutral) OC sorption coefficient (liter kg <sup>-1</sup> )	6070	170	100	650
Anion/cation OC sorption coefficient (liter kg <sup>-1</sup> )			100 000 (cation)	12 (anion)
Kinetic sorption rate constant (h <sup>-1</sup> )	0.002	0	0	0
Freundlich adsorption exponent (1/ <i>n</i> )	1.0	1.0	1.0	1.0
Acid/base dissociation constant			12.3 (p <i>K</i> <sub>b</sub> )	4.6 (p <i>K</i> <sub>a</sub> )
Foliar deposit half-life (days)	2			
Half-life on crop residues (days)	2	3	3	0.2
Soil surface layer half-life (days)	7 (30) <sup>a</sup>	5	20	20
Soil sub-surface half-life (days)	30	15	60	20
Fraction of kinetic sorption sites	0.3	0	0	0
Washoff fraction	0.65	1.0	1.0	0.5
Washoff exponent	0.002	0.013	0.005	0.005

<sup>a</sup> Seven days used for calculations in Figs 2 and 3, and 30 days used for sensitivity base value.

flumetsulam) we input an artificially large decrease in soil pH with depth, of one full unit per horizon, and examined the predicted concentrations of the herbicides in the soil and solution phases, and used these values along with the total of the humus carbon fractions to examine the apparent *K*<sub>oc</sub> values.

The magnitude of output changes resulting from parameter input changes were compared with the magnitude of the input changes. If a selected parameter had simultaneous multiple values (for example, soil saturated hydraulic conductivity has six values, one for each soil horizon) then all the values were varied simultaneously by the same percentage about the base values. The range of parameter variations was determined primarily in preliminary runs according to the sensitivities of selected parameters. The criterion of Lane and Ferreira<sup>4</sup> was used to define whether or not a tested parameter or input variable was sensitive; ie a model parameter or input variable is defined as sensitive if errors in that parameter or input variable result in errors in output variables as large as or larger than the parameter errors. However, we defined the sensitivity index (*S*(*i*)) for parameter or variable *i* as:

$$S_i = \left( \frac{P_i - P_i^b}{P_i^b} \right) \cdot 100 \quad (11)$$

where *P<sub>i</sub>* is the prediction with varying parameter/variable *i* and *P<sub>i</sub><sup>b</sup>* is the same prediction with the corresponding base value.

This sensitivity index is different from the sensitivity coefficient commonly in use, which is a partial derivative representing the change in model outputs resulting from a change in a model input. The problem with the usual sensitivity coefficient is that the magnitude of sensitivity depends on both the dimension and units of parameters. One may calculate sensitivities for two parameters that are numerically equal, however, they may not be dimensionally identical. Thus, simply comparing numerical values (sensitivity coefficients) calculated according to the derivative may be inadequate.

No model calibration was done except for selecting a fitting saturated hydraulic conductivity of surface crusts/seals. Because a large number of parameters were used in the sensitivity analysis, only annual surface water runoff and mean value of runoff from the six artificial rainfall events were compared to determine the sensitivities of parameters for hydrology simulations. Among the hydrology parameters employed in RZWQM, soil-water content at 33 kPa (*θ<sub>f</sub>*), 1500 kPa and at saturation (*θ<sub>s</sub>*), bubbling pressure (*h<sub>b</sub>*), and pore-size distribution index (*λ*) are known to be important parameters in determining surface water runoff. The sensitivity of *h<sub>b</sub>* and *λ* and the effects of soil macropores on surface runoff have been examined for RZWQM<sup>12,46,55</sup> and for a similar model, Opus.<sup>56</sup> The *θ<sub>s</sub>* is not measured but calculated<sup>25</sup> from soil bulk density (*ρ*). Thus, *ρ* could affect runoff prediction. In RZWQM, *θ<sub>s</sub>* and *θ<sub>f</sub>* are used to calculate effective porosity, which is then used to calculate the saturated hydraulic conductivity (*K<sub>s</sub>*) of the soil after tillage.<sup>25</sup> The *K<sub>s</sub>* values of soil matrix and surface crusts/seals are used in the Green–Ampt equation (eqn (1)) and the Richards' equation (eqn (2)) for calculations of water infiltration and redistribution. Therefore, *K<sub>s</sub>* could significantly affect the runoff prediction. The sensitivities of the albedo parameters for dry soil, wet soil and mature crop to runoff were also included in the analyses.

Runoff loads of the pesticides at the edge of the field and residual mass on crop canopy (crop residues), at the soil surface (top 1 cm) and in the soil profile (including top 1 cm) were compared to determine the sensitivities of parameters to pesticide fate and transport simulations. Based on the half-lives of the pesticides in different compartments (Table 2), the endpoints were selected for comparison. The endpoint for comparing sensitivities of parameters to the prediction of pesticide mass on crop canopy (crop residues) was the mass of the pesticide on canopy (crop residues) at 4 days after the last application. The endpoints for other comparisons were predictions at the end of the simulations. All major pesticide input

parameters and sensitive hydrology parameters were examined in the sensitivity analysis.

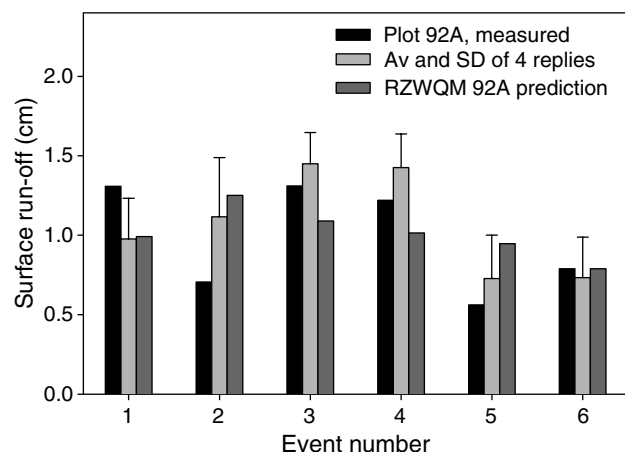
## 4 RESULTS AND DISCUSSION

### 4.1 Simulations of water runoff and chemical fate using base values

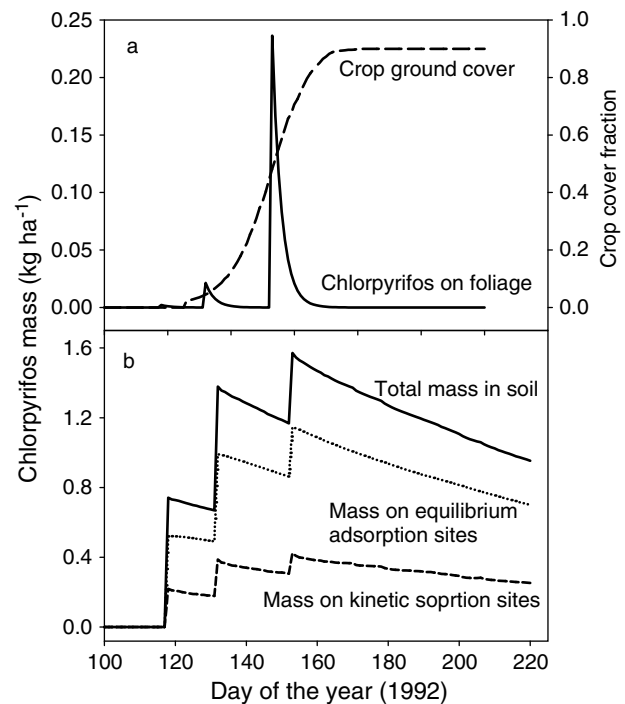
Figure 1 shows the measured and modeled surface water runoff for the six artificial rainfall events from plot 92A using base parameter values from Tables 1 and 2. These predictions can easily be improved with parameter adjustment, but the average relative error was 48%—within a factor of 2. This magnitude of error is considered acceptable given the variety of conditions of the field experiment (ranging from freshly tilled bare soil to complete corn canopy). Figure 1 also shows the measured average and variance of runoff from the four replicate runoff events from the same experiment<sup>47</sup> including plot 92A. The average difference between RZWQM predictions for plot 92A and these measured average runoff amounts is closer: the average relative error was only 18%. These results were considered adequate for sensitivity testing for pesticide losses and no further model calibration was conducted.

Figure 2 shows how RZWQM partitioned chlorpyrifos between corn foliage and soil solid and solution phases. The three peaks in predicted chlorpyrifos amounts on corn canopy and in soil (Fig 2a, b) correspond to three applications of chlorpyrifos to corn plants on April 24, May 11 and June 1 at the four-leaf stage, six-leaf stage and near maturity, respectively. Ground cover estimates by RZWQM are shown on Fig 2a, along with the predicted amounts of chlorpyrifos deposited on corn canopy. Simulated foliar chlorpyrifos residues dissipated rapidly on corn canopy (Fig 2a) in response to foliar washoff and the 2-day half-life used in the simulation.

The remainder of the chlorpyrifos applications deposited on crop residues (not shown) and on the soil (Fig 2b). Because chlorpyrifos sorption coefficient



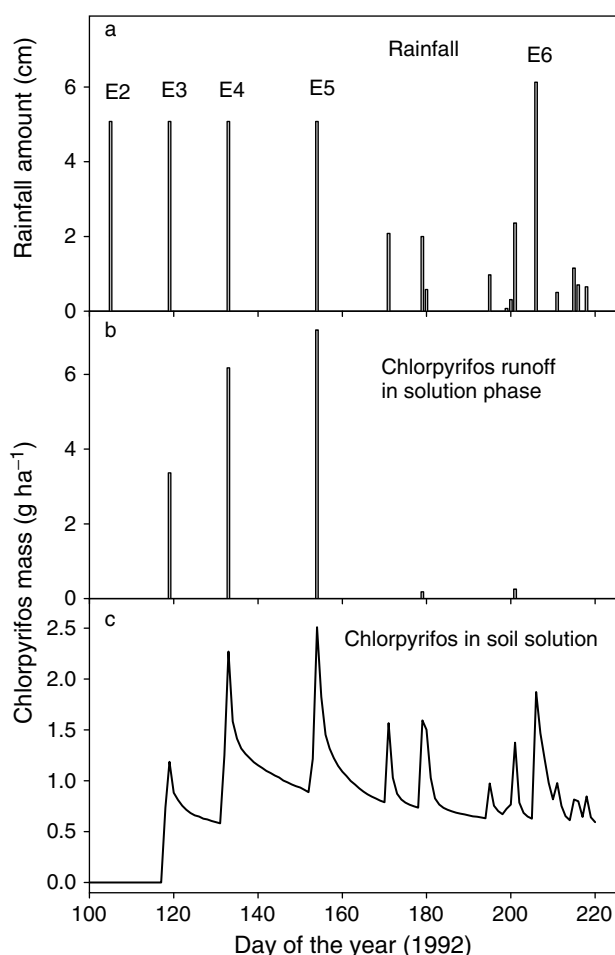
**Figure 1.** Observed and RZWQM-predicted water runoff amounts for plot A, 1992 rainfall simulation events, and averages and standard deviations of measured runoff for similar events for four plots.



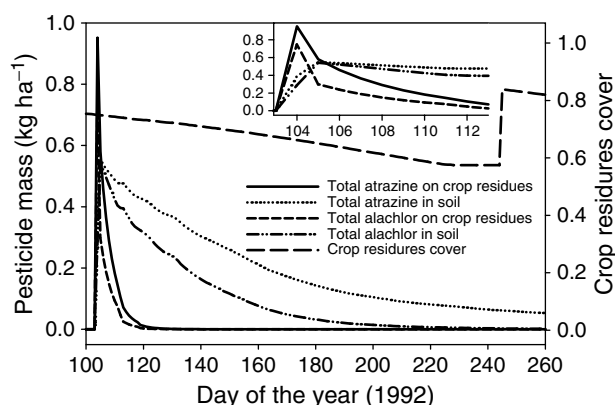
**Figure 2.** Three  $1.12 \text{ kg ha}^{-1}$  applications of chlorpyrifos at two-week intervals to a growing corn canopy result in increasing interception by corn foliage as the corn canopy develops. Un-intercepted chlorpyrifos deposits on soil where it partitions between soil equilibrium and 'kinetic' sorption sites and soil water (dissolved amounts are too small to be seen at this scale, see Fig 3).

( $K_{oc}$ ) is large (Table 2), only a small fraction of chlorpyrifos was predicted in solution and this fraction fluctuated as rainfall and chlorpyrifos were applied to the system (Fig 3c).

We do not have measured chlorpyrifos data to compare with the model simulations. However, in another paper in this series, Ma *et al*<sup>57</sup> showed that RZWQM predictions of runoff of several other pesticides and transformation products matched the measured data well. Since the erosion sub-routine is not activated in the current version of RZWQM, the predictions for the bare-soil and nearly bare-soil runoff Events 3 and 4, respectively, almost certainly underestimated chlorpyrifos runoff losses. It is interesting that, as the canopy got close to full cover in the last 'worst-case' runoff event (Event 5), in which chlorpyrifos was applied 24 h before runoff, chlorpyrifos showed an increase in solution-phase runoff (Fig 3b) (whereas the eroded chlorpyrifos was certainly less because of the high crop cover and less intense interactions between rain drops and surface soil)—this is probably due to the high accumulated chlorpyrifos concentrations at the soil surface after three consecutive applications. Full canopy cover at Event 5 increased chlorpyrifos interceptions on canopy during the application and the subsequent foliar washoff of the intercepted chlorpyrifos also contributed to higher chlorpyrifos runoff. Thus, within these limitations, the model appears to simulate chlorpyrifos behavior in this complex scenario reasonably well.



**Figure 3.** Timing of precipitation events (including rainfall simulation Events 2–6), solution phase chlorpyrifos losses in runoff, and total chlorpyrifos mass in soil solution versus time. Note the release of chlorpyrifos into the soil solution phase as water is added (even though actual solution concentrations would decrease). Compare chlorpyrifos amounts with those in soil and on canopy in Fig 2.



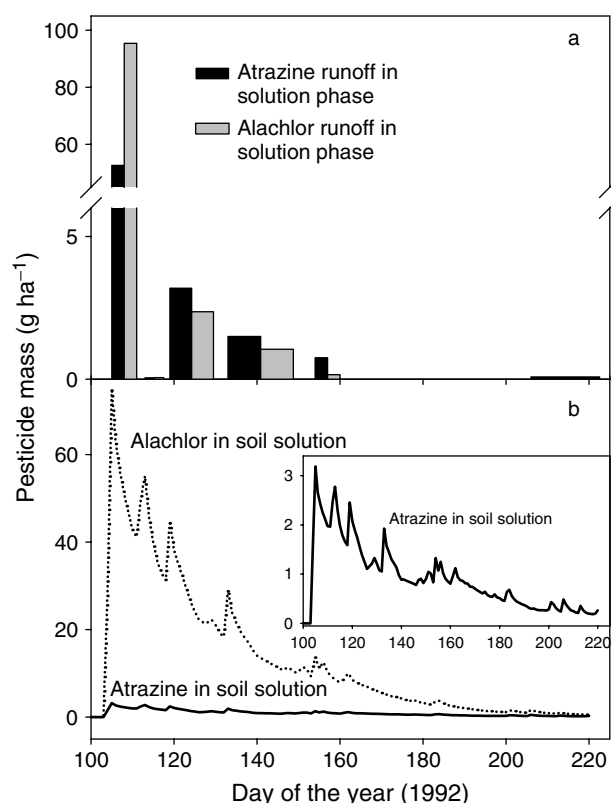
**Figure 4.** Predicted dissipation and distribution of atrazine and alachlor between crop residues and the soil. Note that the crop residue cover decreases slowly as a result of decay and then increases as foliar senescence begins.

Unlike the washoff of the post-emergence applications of chlorpyrifos that primarily occurred on corn canopy, the washoff of the pre-emergence applications of alachlor and atrazine occurred on corn residues (Fig 4). Based on the mass of corn residues

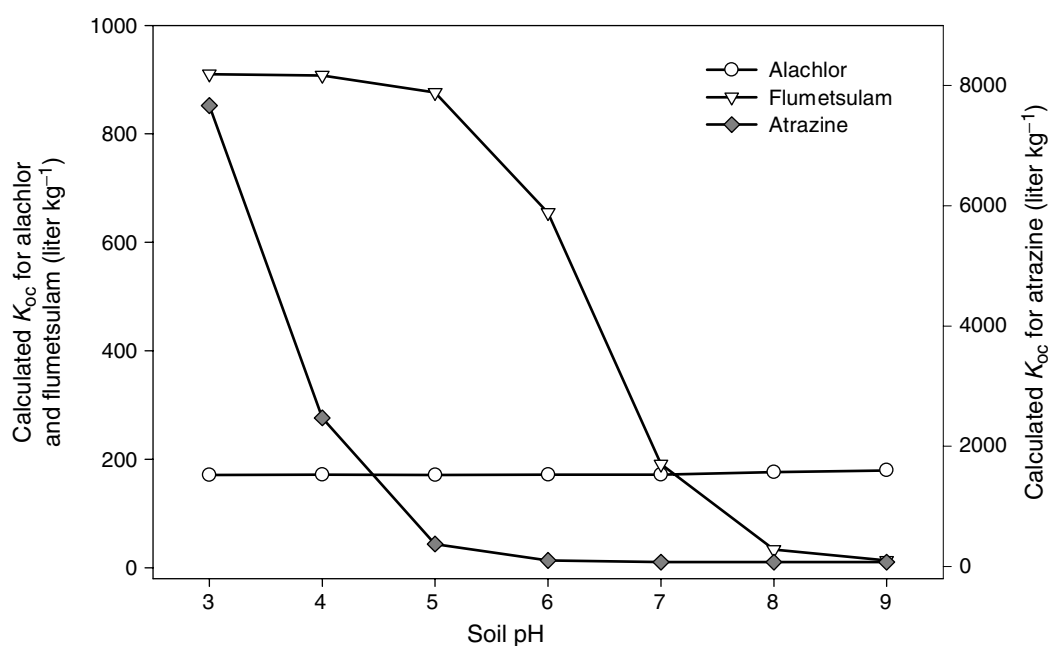
(10 tonne  $\text{ha}^{-1}$ ) at the beginning of the simulation, RZWQM predicted that 72% and 71% of surface-applied alachlor and atrazine, respectively, were intercepted during the applications. Pesticide intercepted on corn residues dissipated rapidly as a result of short half-lives (Table 2) and washoff to soil surface by rainfalls. This is especially obvious for alachlor (Fig 4) because of its higher washoff exponent (Table 2).

Data in Fig 5 show the simulated mass of alachlor and atrazine in surface water runoff and in soil solution. Unlike the runoff loss of the multiply applied chlorpyrifos in water (Fig 3b), the runoff loss of single-applied alachlor and atrazine in water decreased monotonically with time (Fig 5a). As with chlorpyrifos (Fig 3c), the mass of alachlor and atrazine in soil solution (Fig 5b) fluctuated as a result of the release of the herbicides into the soil solution (desorption) as water was added.

The predicted pH dependence of the sorption of the three herbicides is shown in Fig 6. Alachlor, a neutral molecule, shows no pH dependence. For acidic flumetsulam and basic atrazine, if reasonable values of  $\text{p}K_a$  or  $\text{p}K_b$  and the neutral and ionic species are input (Table 2), then the predicted herbicide soil–water partitioning appears to follow the correct pattern—note that the ‘near-surface’ pH correction of  $-1.8$  units means that the shift to the higher-sorbing species occurs at about 2 pH units above the  $\text{p}K$  value. However, we discovered that (a) non-zero kinetic parameters appear to affect the overall  $K_{oc}$  value, and thus all were set to zero to obtain the values



**Figure 5.** (a) Atrazine and alachlor solution phase losses in runoff and (b) herbicide mass in soil solution versus time.



Depth (cm)	Total OC	Alachlor conc of		Atrazine conc of		Flumetsulam conc of		Soil pH	Alachlor		Atrazine		Flumetsulam	
	pools ( $\mu\text{g C g}^{-1}$ )	Adsorbed ( $\mu\text{g g}^{-1}$ )	In soln ( $\text{mg liter}^{-1}$ )	Adsorbed ( $\mu\text{g g}^{-1}$ )	In soln ( $\text{mg liter}^{-1}$ )	Adsorbed ( $\mu\text{g g}^{-1}$ )	In soln ( $\text{mg liter}^{-1}$ )		$K_d$ liter $\text{kg}^{-1}$	$K_{oc}$ liter $\text{kg}^{-1}$	$K_d$ liter $\text{kg}^{-1}$	$K_{oc}$ liter $\text{kg}^{-1}$	$K_d$ liter $\text{kg}^{-1}$	$K_{oc}$ liter $\text{kg}^{-1}$
1	7981.39	2.10	1.47	1.47	2.54	0.02	0.21	9	1.43	180	0.58	73	0.10	13
9	7928.24	4.14E-02	0.03	0.30	0.53	0.02	0.09	8	1.40	176	0.57	72	0.26	33
34	3321.04	6.05E-08	1.1E-07	2.11E-05	8.8E-05	6.05E-05	9.5E-05	7	0.57	171	0.24	72	0.63	191
73	2347.84	3.41E-14	8.5E-14	1.59E-10	6.72E-10	3.35E-11	2.2E-11	6	0.40	171	0.24	101	1.54	654
101	1202.96	4.49E-20	2.2E-19	9.64E-16	2.13E-15	1.98E-18	1.9E-18	5	0.21	171	0.45	376	1.05	876
121	194.51	3.86E-25	1.2E-23	1.02E-20	2.12E-20	3.06E-24	1.7E-23	4	0.03	171	0.48	2471	0.18	908
152	97.31	7.59E-34	4.6E-32	1.26E-30	1.69E-30	1.49E-33	1.7E-32	3	0.02	171	0.75	7667	0.09	910

**Figure 6.** Calculated apparent soil sorption coefficients  $K_d$  and organic carbon sorption coefficients  $K_{oc}$  using solution and sorbed concentrations and organic matter content extracted from the RZWQM output file 'layer.plt' for day 114 and with artificial input of pH decreasing from 9 to 3 with depth. Alachlor, a neutral molecule, shows no pH dependence; acidic flumetsulam and basic atrazine exhibit the correct pH dependence.

in Fig 6; this requires more investigation and may require a model fix; (b) allowing the model to attempt to estimate the neutral species  $K_{oc}$  from inputting only  $pK$  and observed  $K_{oc}$  at a reference pH does not appear to be working properly. Sensitivity analysis for flumetsulam  $K_{oc}$  below also indicates potential problems of this process simulation. Thus, we caution that a clarification of the best procedure for inputting data for ionizable compounds is needed.

#### 4.2 Sensitivity of predicted water runoff to hydrology parameters

Parameters tested for sensitivity for predicted surface water runoff are given in Table 3. Of the eight parameters/variables analyzed for sensitivity to surface water runoff prediction (Table 3), soil water content at 33 kPa ( $\theta_f$ ), soil bulk density ( $\rho$ ), the saturated hydraulic conductivity of surface crusts/seals ( $K_s^c$ ), and rainfall were identified as sensitive parameters based on the sensitivity criterion (eqn (11)). These parameters played critical roles in the runoff simulation. Therefore, efforts and resources should be spent on

quantifying these parameters for accurate and reliable runoff prediction. Albedos of the soil and crop were insensitive parameters for runoff prediction, as might be expected, although there was a small response. Increasing  $\rho$  is expected to increase surface runoff and vice versa. However, the opposite was observed (Table 3). This is probably due to the interactions among  $\rho$ , soil porosity ( $\Phi$ ), and  $\theta_s$ , as described previously. This could also result from the limitations of the 'local' sensitivity analysis approach that only allows for one model input to change at a time. Because  $\Phi$  is inversely related to  $\rho$ , when  $\rho$  increases, the model internally calculated  $\Phi$  decreases. When the calculated  $\Phi$  goes below the user-input  $\theta_s$ , then a problem occurs. More investigation into this problem is needed.

The soil saturated hydraulic conductivity ( $K_s$ ) was expected to be a sensitive parameter, but it turned out to be rather insensitive (Table 3). A close examination of the program revealed that the insensitivity of the soil  $K_s$  in this case was caused by the formation of surface crusts/seals, which had a much smaller hydraulic conductivity than that of the soil surface



**Table 3.** Sensitivities of event and annual water runoff to parameter variation

Parameter	Base value	Variation (% of base value)	Event runoff mean (cm)	Change in event runoff mean (%)	Annual runoff (cm)	Change in annual runoff (%)
	Base run	0	1.01	0	13.19	0
Soil-water content at 33 kPa	Table 1	−10	1.87	85	23.59	79
		+10	0.37	−64	5.80	−56
Soil bulk density	Table 1	−10	1.74	72	22.67	72
		+10	0.11	−89	3.66	−72
Soil saturated hydraulic conductivity	Table 1	−10	1.13	12	13.72	4
		+10	1.04	3	12.72	−4
Soil crust saturated hydraulic conductivity (cm h <sup>−1</sup> )	0.7 × 10 <sup>−2</sup>	−10	1.23	22	14.82	12
		+10	0.95	−6	11.78	−11
Albedo of dry soil	0.25	−50	1.07	6	13.10	−0.7
		+50	1.09	8	13.28	0.7
Albedo of wet soil	0.10	−50	1.07	6	13.18	−0.08
		+50	1.09	8	13.20	0.1
Albedo of mature crop	0.35	−50	1.07	6	13.09	−0.8
		+50	1.09	8	13.31	0.9
Daily rainfall amount	Measured	−10	0.68	−33	8.65	−34
		+10	1.52	51	18.49	40

horizon (Table 1). In RZWQM, the mean  $K_s$  of the wetting soil profile for a homogeneous soil or the surface layer of a layered soil is assumed to be the field saturated hydraulic conductivity, while the mean  $K_s$  of the wetting soil profile for a layered soil with the  $K_s$  decreasing with depth is equal to the harmonic mean of the  $K_s$  of the wetted zone(s). However, if the  $K_s$  of the subsoil layer in a layered soil is greater than that of the harmonic mean above it, the harmonic mean of the  $K_s$  of the wetting soil profile will govern the flow in the subsoil layer. Thus, the surface crust hydraulic conductivity plays a dominant role in determining water infiltration and runoff at the soil surface. A test simulation indicated that surface water runoff prediction would be very sensitive to  $K_s$  had surface crusts/seals not existed (data not shown). This is a good example of a case where the sensitivity of one parameter may be masked by another.

#### 4.3 Sensitivity of predicted pesticide mass and runoff loads

Data in Table 4 summarize the sensitivities of predictions of chlorpyrifos mass on crop canopy (crop residues), at the soil surface, in the soil profile and in runoff, to selected parameters. Some parameter sensitivities are obvious and are as expected; some others may need explanations because of the parameter interactions, which affect the sensitivity index calculations. Chlorpyrifos on crop canopy (crop residues) was only sensitive to input foliar (crop residues) half-life (Table 4). A small sensitivity of chlorpyrifos on foliage to temperature is observed: a 2°C change in temperature resulted in a 0.5% change in predicted chlorpyrifos mass on canopy. This

might be caused by pesticide volatilization simulation since RZWQM calculates pesticide volatilization when the pesticide vapor pressure and water solubility are provided.

The prediction of chlorpyrifos mass at the soil surface was sensitive to the fraction of kinetic sorption sites ( $1-F$ ), the Freundlich exponent ( $1/n$ ), rainfall,  $\theta_f$ ,  $\rho$ , chlorpyrifos half-life at the soil surface and air temperature, and nearly sensitive to soil organic carbon content (Table 4). The chlorpyrifos  $K_{oc}$  was expected to be a sensitive parameter. This was not observed because the sensitivity of  $K_{oc}$  was masked by that of the fraction of kinetic sorption sites of the two-site sorption model. When the instantaneous equilibrium adsorption model (eqn (9)) is used, as demonstrated below for flumetsulam, the prediction is sensitive to  $K_{oc}$ . Notice that a 25% decrease in  $1/n$  resulted in a 37% increase in chlorpyrifos mass at the soil surface while a 25% increase in  $1/n$  only resulted in a 0.07% increase (Table 4)—this is an example of extrapolating the Freundlich equation into regions of high concentrations. The prediction of chlorpyrifos mass in the soil profile was much less sensitive to  $1/n$ , but was sensitive to half-life in the surface layer (Table 4). This occurred because more than 66% of the total chlorpyrifos in soil was still in the top 1 cm at the end of the simulation. In addition, the prediction of chlorpyrifos mass in the soil profile was sensitive to  $\theta_f$ ,  $1-F$ ,  $\rho$  and air temperature. Like the sensitivity of  $K_{oc}$  at the soil surface, the sensitivity of  $K_{oc}$  in the soil profile was also masked by the fraction of kinetic sorption sites.

The prediction of chlorpyrifos annual load in surface water runoff was sensitive to rainfall,  $\theta_f$ ,  $\rho$ , and  $K_s^c$  (Table 4). It was expected that runoff

**Table 4.** Sensitivities of chlorpyrifos mass on crop canopy (crop residues), at the soil surface and in the soil profile and annual runoff load total to various input parameters

Parameter	Chlorpyrifos sensitivity index (%)					
	Base value	Variation (%)	Crop canopy/ crop residues	Soil surface	Soil profile	Annual runoff mass
Runoff mixing coefficient ( $\text{cm}^{-1}$ )	4.4	−25 +25	— <sup>a</sup>	−0.3 0.3	−0.3 0.2	12 −7
Walker soil moisture power factor	−0.8	−25 +25	—	−4 4	−4 4	−0.1 0.2
Soil organic carbon content	Table 1	−25 +25	—	−24 20	−0.5 0.4	8 −5
Activation energy for pesticide degradation ( $\text{kJ mole}^{-1}$ )	54.0	−25 +25	—	−12 10	−12 11	−0.1 0.2
Fraction of soil kinetic sorption sites	Table 2	−25 +25	—	−25 31	−25 31	−0.5 0.6
Foliar half-life	Table 2	−10 +10	−11 +11	−0.1 0.3	−0.2 0.2	−0.7 0.4
Half-life on crop residues	Table 2	−10 +10	−20 20	−0.6 0.6	−0.6 0.6	−5 4
Foliar washoff fraction	Table 2	−25 +25	0.4 −0.4	−0.7 0.9	−0.8 0.8	−4 4
Foliar washoff power parameter	Table 2	−25 +25	0.4 −0.4	−0.7 0.9	−0.8 0.8	−4 4
Soil organic carbon sorption coefficient	Table 2	−25 +25	—	−12 8	−0.3 0.2	5 −3
Freundlich $1/n$	1.0	−25 +25	—	37 0.07	−8 0	−11 0
Daily rainfall amounts	Measured	−10 +10	0.4 −0.3	12 −9	8 −7	−40 44
Soil-water content at 33 kPa	Table 1	−10 +10	—	−9 14	−11 16	85 −70
Soil saturated hydraulic conductivity	Table 1	−10 +10	—	−2 2	−2 2	5 −4
Soil bulk density <sup>b</sup>	Table 1	−10 +10	—	−26 53	−26 53	78 −89
Soil crust saturated hydraulic Conductivity ( $\text{cm h}^{-1}$ )	$0.7 \times 10^{-2}$	−10 +10	—	0.6 −0.7	0.1 −0.6	15 −13
Kinetic sorption rate constant	Table 2	−25 +25	—	9 −5	6 −4	−0.1 0.04
Half-life on soil surface	Table 2	−10 +10	—	−20 21	−17 17	−0.5 0.5
Daily average air temperature	Measured	−2 +2	0.04 −1	22 −17	23 −18	3 −3
Half-life in lower soil layers	Table 2	−10 +10	—	−0.2 0.2	−4 4	0.04 0.04

<sup>a</sup> — indicates no dependence, as expected.

<sup>b</sup> The endpoint for determining the sensitivity index was at 271 days after the start of the simulation because the model stopped running after this date when the soil bulk density had increased by 10% of its base value. This could be a potential problem.

load of chlorpyrifos would be sensitive to the mixing factor  $B$  (eqn (8)), but this was not observed in this scenario.

The relatively high sensitivities of  $\theta_f$ ,  $\rho$ , and rainfall for predictions of chlorpyrifos mass in soil and in surface water runoff (Table 4) suggest that accurate predictions of pesticide fate depend on the pesticide physical and chemical properties as well as some soil and environmental factors.

Data in Table 5 show the sensitive parameters/variables for predictions of flumetsulam behaviour. As for chlorpyrifos, the prediction of

flumetsulam mass at the soil surface was sensitive to  $\theta_f$ ,  $\rho$ ,  $1/n$ , rainfall, and air temperature. In addition, the prediction was also very sensitive to soil pH,  $pK_a$ , and the neutral molecule  $K_{oc}$ . Note that both increasing and decreasing the neutral molecule  $K_{oc}$  by 25% resulted in high and negative sensitivity indices (Table 5). It is expected that increasing the neutral molecule  $K_{oc}$  would result in a positive sensitivity index (eqn (11)) because the same flumetsulam half-life was assigned to both the soil surface layer and the sub-surface layers (Table 2). This process apparently needs further investigation, as discussed previously.

**Table 5.** Sensitivities of flumetsulam mass on crop residues, at the soil surface, and in the soil profile and annual runoff load total to various input parameters

Parameter	Flumetsulam sensitivity index (%)					
	Base value	Variation (%)	Crop residues	Soil surface	Soil profile	Annual runoff mass
Soil layer pH	Table 1	+2 units	— <sup>a</sup>	−100	−6	554
		+4 units		−100	−48	396
pK <sub>a</sub>	Table 2	−25	—	−92	−4	239
		+25		−93	−4	254
Soil-water content at 33 kPa	Table 1	−10	—	−19	−25	80
		+10		41	48	−68
Soil saturated hydraulic conductivity	Table 1	−10	—	−5	−5	4
		+10		4	4	−4
Soil bulk density <sup>b</sup>	Table 1	−10	—	−58	−58	83
		+10		228	226	−87
Soil crust saturated hydraulic conductivity	Table 1	−10	—	2	1	14
		+10		−2	−2	−13
Soil organic carbon sorption coefficient	Table 2	−25	—	−97	−5	325
		+25		−88	−4	201
Freundlich 1/ <i>n</i>	1.0	−25	—	136	−0.6	−4
		+25		−0.6	−0.4	0
Daily rainfall amounts	Measured	−10	1	34	23	−39
		+10	−1	−96	−22	393
Daily average air temperature	Measured	−2	2	82	83	0.7
		+2	−2	−49	−49	−2

<sup>a</sup> — indicates no dependence, as expected.

<sup>b</sup> The endpoint for determining the sensitivity index was at 271 days after the start of the simulation because the model stopped running after this date when the soil bulk density had increased by 10% of its base value. This could be a potential problem.

The prediction of flumetsulam mass in the soil profile was sensitive to soil pH (though to a lesser extent than that at the soil surface),  $\theta_f$ ,  $\rho$ , rainfall and air temperature (Table 5). The prediction of flumetsulam mass in surface water runoff was sensitive to all parameters/variables in Table 5 except soil  $K_s$ ,  $1/n$  and air temperature.

Figure 7 shows flumetsulam distribution in the soil profile as affected by soil pH. A 2-unit increase in soil pH moved the solute leading front ( $\sim 1.11 \times 10^{-4} \text{ mg kg}^{-1}$ ) from 4 cm to 7 cm at 7 days after flumetsulam application, while a 4-unit increase in

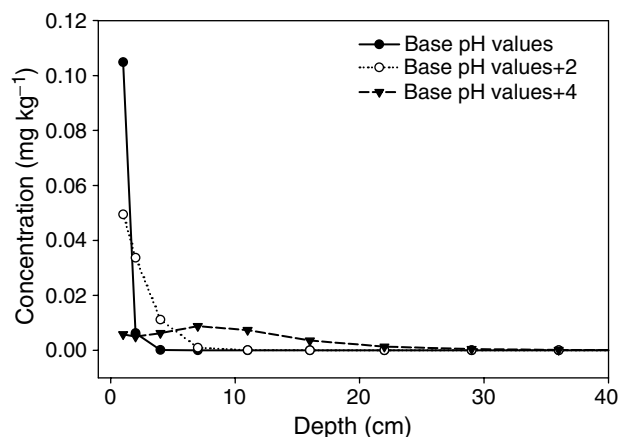
soil pH further moved the front to 36 cm. This is consistent with observations by Fontaine *et al.*<sup>54</sup>

Sensitivities of predictions of alachlor and atrazine were not analyzed. It is expected that the sensitivities of chlorpyrifos predictions should reflect those of alachlor; while the sensitivities of flumetsulam predictions should reflect those of atrazine except with  $pK_a$  replaced by  $pK_b$ .

## 5 CONCLUSIONS

The sensitive parameters identified in this study are in general agreement with those found for Opus<sup>56</sup> and CREAMS.<sup>4</sup> We are encouraged that the RZWQM appears to be well behaved at describing two important but complex processes—foliar deposition and washoff, and sorption of weakly acidic or basic pesticides. It is better to have a not-very-exact description of an important and sometimes dominant process, such as each of these, which are not well described by the current models, than to ignore their effects. The sensitivities of runoff and pesticide fate in soil to input parameters are generally as expected. However, more research is needed to evaluate such processes as soil bulk density changes and kinetic sorption of charged pesticides on water movement and pesticide fate and transport.

There are other important processes in RZWQM that need verification with the field experiments to fill data gaps. These include metabolite transformation and tracking, bound residue formation and the



**Figure 7.** Effects of soil pH on flumetsulam distribution in the soil profile 7 days after application, including 5 cm rain 24 h after flumetsulam application.

behavior of pesticides at the soil/air interface. Some of these processes are tested in an accompanying paper.<sup>57</sup>

## REFERENCES

- Jiao JJ and Lerner DN, Using sensitivity analysis to assist parameter zonation in ground water flow model. *Water Resour Bull* 32:75–87 (1996).
- Rogers CCM, Beven KJ, Morris EM and Anderson MG, Sensitivity analysis, calibration and predictive uncertainty of the Institute of Hydrology distributed models. *J Hydrol* 81:179–191 (1985).
- Knisel WG (ed) *CREAMS—a field scale model for chemical, runoff, erosion from agricultural management systems*, USDA Conserv Res Report No 26, USDA, Washington, DC (1980).
- Lane LJ and Ferreira VA, Sensitivity analysis, in *CREAMS—a field scale model for chemical, runoff, erosion from agricultural management systems*. Ed by Knisel WG, USDA Conserv Res Report No 26, USDA, Washington, DC, pp 113–158 (1980).
- Renard KG and Ferreira VA, RUSLE model description and database sensitivity. *J Environ Qual* 22:458–466 (1993).
- Johnson RC, Imhoff JC, Davis HH Jr, Kittle JL Jr and Donigan AS, User's manual for the Hydrological Simulation Program-Fortran (HSPF), US Environmental Protection Agency Report EPA 600/3-84-066, 767 pp (1984).
- Fontaine TA and Jacomino VMF, Sensitivity analysis of simulated contaminated sediment transport. *J Am Water Resour Assoc* 33:313–326 (1997).
- Fontaine DD, Havens PL, Blau GE and Tillotson PM, The role of sensitivity analysis in groundwater risk modeling for pesticides. *Weed Technol* 6:716–724 (1992).
- Soutter M and Musy A, Global sensitivity analyses of three pesticide leaching models using a Monte-Carlo Approach. *J Environ Qual* 28:1290–1297 (1999).
- Carsel RF and Parrish RS, Developing joint probability distributions of soil water retention characteristics. *Water Resources Res* 24:755–769 (1988).
- Ahuja LR, Rojas KW, Hanson JD, Shaffer MJ and Ma L (Eds), *Root Zone Water Quality Model—Modeling management effects on water quality and crop production*, Water Resources Publications LLC, Highlands Ranch, CO (1999).
- Malone RW, Ma L, Wauchope RD, Ahuja L, Rojas KW, Ma Q, Warner R and Byers M, Modeling hydrology, metribuzin degradation and metribuzin transport in macroporous tilled and no-till silt loam using RZWQM. *Pest Manag Sci* 60:253–266 (2004).
- Boesten JJTI, Sensitivity analysis of a mathematical model for pesticide leaching to groundwater. *Pestic Sci* 31:375–388 (1991).
- Giambelluca TW, Loague K, Green RE and Nullet MA, Uncertainty in recharge estimation: Impacts on groundwater vulnerability assessments for the Pearl Harbor Basin, Oahu, Hawaii, USA. *J Contam Hydrol* 23:85–112 (1996).
- Persicani D, Pesticide leaching into field soils: sensitivity analysis of four mathematical models. *Ecol Model* 84:265–280 (1996).
- Wauchope RD, Rojas KW, Ahuja LR, Ma Q, Malone RW and Ma L, Documenting the pesticide processes module of the ARS RZWQM agroecosystem model. *Pest Manag Sci* 60:222–239 (2004).
- Green WH and Ampt GA, Studies on soil physics. 1. Flow of air and water through soils. *J Agric Sci* 4:1–24 (1911).
- Ahuja LR, Modeling infiltration into crusted soils by the Green-Ampt approach. *Soil Sci Soc Am J* 47:412–418 (1983).
- Ahuja LR, Johnsen KE and Heathman GC, Macropore transport of a surface-applied bromide tracer: Model evaluation and refinement. *Soil Sci Soc Am J* 59:1234–1241 (1995).
- Swartzendruber D, Rigorous derivation and interpretation of the Green and Ampt equation, in *Proc Intern Conf Infiltration Development and Applications*, ed by Fok YS, Water Resour Res Center, Univ of Hawaii, Honolulu, HI, pp 28–37 (1987).
- Bouwer H, Infiltration of water into a nonuniform soil. *J Irrig Drain Div Amer Soc Civil Eng* 95:451–462 (1969).
- Morel-Seytoux HJ and Khanji J, Derivation of an equation of infiltration. *Water Resour Res* 10:795–800 (1974).
- Brakensiek DL and Onstad CA, Parameter estimation of the Green and Ampt infiltration equation. *Water Resour Res* 13:1009–1012 (1977).
- Ahuja LR, DeCoursey DG, Barnes BB and Rojas KW, Characteristics of macropore transport studied with the ARS Root Zone Water Quality Model. *Trans ASAE* 36:369–380 (1985).
- Ahuja LR, Johnsen KE and Rojas KW, Water and chemical transport in soil matrix and macropores, in *Root Zone Water Quality Model—Modeling management effects on water quality and crop production*, ed by Ahuja LR, Rojas KW, Hanson JD, Shaffer MJ and Ma L. Water Resource Publ LLC, Highlands Ranch CO, pp 13–50 (1999).
- Celia MA, Bouloutaas ET and Zarba RL, A general mass-conservative numerical solution for the unsaturated flow equation. *Water Resour Res* 26:1483–1496 (1990).
- Nimah M and Hanks RJ, Model for estimating soil–water–plant–atmospheric interrelation: I. Description and sensitivity. *Soil Sci Soc Am Proc* 37:522–527 (1973).
- Brooks RH and Corey AT, Hydraulic properties of porous media, Hydrology paper No 3, Colorado State University, Fort Collins, CO (1964).
- Ahuja LR, Naney JW and Williams RD, Estimating soil water characteristics from simpler soil properties or limited data. *Soil Sci Soc Am J* 49:1100–1105 (1985).
- Rawls WJ, Brakensiek DL and Saxton KE, Estimation of water properties. *Trans Am Soc Agric Eng* 25:1316–1320, 1328 (1982).
- Ahuja LR, Cassel DK, Bruce RR and Barnes BB, Evaluation of spatial distribution of hydraulic conductivity using effective porosity data. *Soil Sci* 148:404–411 (1989).
- Campbell GS, A simple method for determining unsaturated conductivity from moisture retention data. *Soil Sci* 117:311–314 (1974).
- Shuttleworth WJ and Wallace JS, Evaporation from sparse crops—an energy combination theory. *Quart J Roy Meteorol Soc* 3:839–855 (1985).
- Farahani HJ and DeCoursey DG, Potential evaporation and transpiration processes in the soil-residue-canopy system, in *Root Zone Water Quality Model—Modeling management effects on water quality and crop production*, ed by Ahuja LR, Rojas KW, Hanson JD, Shaffer MJ and Ma L. Water Resource Publ LLC, Highlands Ranch, CO, pp 51–80 (1999).
- Walker A, A simulation model for prediction of herbicide persistence. *J Environ Qual* 3:396–401 (1974).
- Walker A, Helwig A and Jacobsen OS, Temperature and pesticide degradation, in *Soil persistence models and EU registration*, FOCUS documentation, URL <http://viso.ei.jrc.it/focus/>, Chapter 1, pp 9–20, (1996).
- Willis GH, McDowell LL, Meyer LD and Southwick LM, Toxaphene washoff from cotton plants by simulated rainfall. *Trans Am Soc Agric Eng* 25:642–646 (1982).
- Ahuja LR, Characterization and modeling of chemical transfer to runoff. *Adv Soil Sci* 4:149–188 (1986).
- Heathman GC, Ahuja LR and Baker JL, Test of a non-uniform mixing model for transfer of herbicides to surface runoff. *Trans Am Soc Agric Eng* 39:450–455 (1986).
- Selim HM, Davidson JM and Mansell RS, Evaluation of a two-site adsorption-desorption model for describing solute transport in soils, Summer computer conference, July 12–14, Washington, DC (1976).
- Cameron DR and Klute A, Convective-dispersive solute transport with a combined equilibrium and kinetic adsorption model. *Water Resour Res* 13:183–188 (1977).
- Boesten JJTI, van del Pas LJ and Smelt H, Field test of a mathematical model for non-equilibrium transport of pesticides in soil. *Pestic Sci* 25:187–203 (1989).
- Ma QL, Ahuja LR, Wauchope RD, Benjamin JG and Burgoa B, Comparison of instantaneous equilibrium and equilibrium-kinetic sorption models for simulating simultaneous leaching and runoff of pesticides. *Soil Sci* 161:646–655 (1996).

- 44 Nicholls PH and Evans AA, Sorption of ionisable organic compounds by field soils. Part 1: acids. *Pestic Sci* **33**:319–330 (1991).
- 45 Nicholls PH and Evans AA, Sorption of ionisable organic compounds by field soils. Part 2: cations, bases, and zwitterions. *Pestic Sci* **33**:331–345 (1991).
- 46 Ma QL, Wauchope RD, Hook JE, Johnson AW, Truman CC, Dowler CC, Gascho GJ, Davis JG, Sumner HR and Chandler LD, Influence of tractor wheel tracks and crusts/seals on runoff from a coastal plain loamy sand: observations and simulations with the RZWQM model. *Agric Sys* **5**:77–100 (1998).
- 47 Wauchope RD, Sumner HR, Truman CC, Johnson AW, Dowler CC, Hook JE, Gascho GJ, Davis JG and Chandler LC, Runoff from a cornfield as affected by tillage and corn canopy: a large-scale simulated-rainfall hydrologic data set for model-testing. *Water Resour Res* **35**:2882–2885 (1999).
- 48 Sumner HR, Wauchope RD, Truman CC, Dowler CC and Hook JE, Rainfall simulator and plot design for mesoplot runoff studies. *Trans Am Soc Agric Eng* **39**:125–130 (1996).
- 49 Radcliffe DE, West LT, Hubbard RK and Asmussen LE, Surface sealing in Coastal Plains loamy sands, *Soil Sci Soc Am J* **55**:223–227 (1991).
- 50 Perkins HF, Hook JE and Barbour NW, Soil characteristics of selected areas of the Coastal Plain Experiment Station and ABAC Research Farms, Research Bulletin 346, The Georgia Agricultural Experiment Stations, College of Agriculture, The University of Georgia (1986).
- 51 Wauchope RD, Buttler TM, Hornsby AG, Augustijn-Beckers PWM and Burt JP, The SCS/ARS/CES pesticide properties database for environmental decision-making. *Rev Environ Contam Toxicol* **123**:1–164 (1992).
- 52 Getzin LW, Factors influencing the persistence and effectiveness of chlorpyrifos in soil. *J Econ Entomol* **78**:412–418 (1985).
- 53 Ma QL, A systematic evaluation of pesticide runoff from a corn field and a golf course fairway: experimental assessment versus GLEAMS, Opus, PRZM-2, and RZWQM model simulations, *PhD Dissertation*, University of Georgia (1998).
- 54 Fontaine DD, Lehmann RG and Miller JR, Soil adsorption of neutral and anionic forms of a sulfoamide herbicide, flumetsulam. *J Environ Qual* **20**:759–762 (1991).
- 55 Malone RW, Ahuja LR, Ma L, Wauchope RD, Ma Q and Rojas KW, Application of the Root Zone Water Quality Model (RZWQM) to pesticide fate and transport: an overview. *Pest Manag Sci* **60**:205–221 (2004).
- 56 Smith RE, Opus: an integrated simulation model for transport of nonpoint-source pollutants at the field scale: Volume I, Documentation, USDA Agric Res Service Publ ARS-98, 120 pp (1992).
- 57 Ma Q, Wauchope RD, Ma L, Rojas KW, Malone RW and Ahuja LR, Test of the Root Zone Water Quality Model (RZWQM) for predicting runoff of atrazine, alachlor and fenamiphos species from conventional-tillage corn mesoplots. *Pest Manag Sci* **60**:267–276 (2004).